THE DISSOLVED NITROGEN FLUFFINESS OF TITAN LAKES. Michael J. Malaska[1], Robert Hodyss[1], Jonathan I. Lunine[2], Alex G. Hayes[2], Jason Hofgartner[1], Gigja Hollyday[3]. [1]Jet Propulsion Laboratory / California Institute of Technology, Pasadena, CA. [2]Cornell University, Ithaca, NY. [3]University of Redlands, Redlands, CA. (Michael.J.Malaska@jpl.nasa.gov)

Introduction: One of the largest surprises of the Cassini mission was the detection of lakes and seas of hydrocarbon liquids on the surface of Saturn's moon Titan (Figure 1) [1]. Titan has surface temperatures that range from 95 K at the equator to 91 K in the polar regions, where the lakes are found. At these cryogenic temperatures, only methane, ethane, propane, and 1-butene (among hydrocarbons) can exist as liquids. While previous models [2-5] suggested that surface liquids on Titan would be composed of ethane, recent observations coupled with laboratory data have been able to constrain the composition of Ligea Mare as being dominated by methane [6,7]. In contrast, lakes in the southern hemisphere, such as Ontario Lacus, are likely more ethane-rich [8].

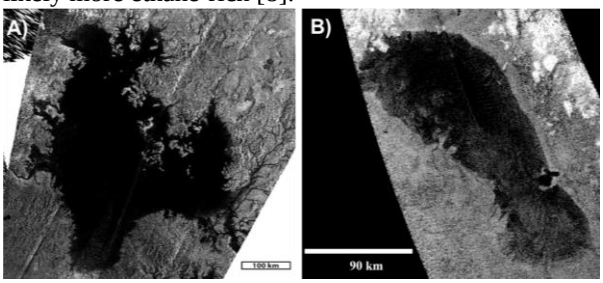

Figure 1. SAR images of Titan lakes: A) Ligeia Mare, Titan, (79°N, 248°W) is located in Titan's north polar region and is thought to be methane-rich. B) Ontario Lacus, Titan, (72°S, 183°W) is located in Titan's south polar region and is thought to contain more ethane than Ligeia Mare.

Titan's thick 1.5 bar atmosphere is composed of 95% nitrogen (N_2) and 5% methane (CH_4). At cryogenic temperatures, significant amounts of nitrogen gas (N_2) can dissolve into the lake fluids. Theoretical models have predicted the amount of nitrogen that will dissolve, but these were based on limited experimental data in Titan's temperature range [2-5]. Our goal was to experimentally determine the amount of nitrogen that dissolved in varying mixtures of methane and ethane at Titan-relevant temperatures and pressures and determine the implications for Titan lake properties.

Materials and Methods: We developed an apparatus that consists of a pressure vessel held inside a cryogenic bath. This is an adaptation of the cooling system previously described in Malaska and Hodyss, 2014 [9]. The pressure vessel is connected by a valve to a gas mixing chamber and a gas manifold that allows the introduction of various gases. In a typical experiment, the desired quanities of hydrocarbon gases are measured by pressure, then transferred and condensed into the pressure vessel at cryogenic temperature. Next, a measured quantity of nitrogen gas is introduced and the drop in system pressure recorded. Once the effects of cooling are taken into account, the pressure drop due to the dissolution of nitrogen into the cryogenic hydrocarbon mixture is determined.

Results: We found that nitrogen dissolves quickly into the cryogenic fluids and was able to rapidly reach equilibrium. In pure methane, the amount of dissolved nitrogen increases at lower temperatures and is 0.2 mole fraction at 91 K (Figure 2). In pure ethane, the amount of dissolved nitrogen also increases at lower temperatures, but the overall amount is lower than for pure methane. Only 0.04 mole fraction of nitrogen dissolves in ethane at 91 K.

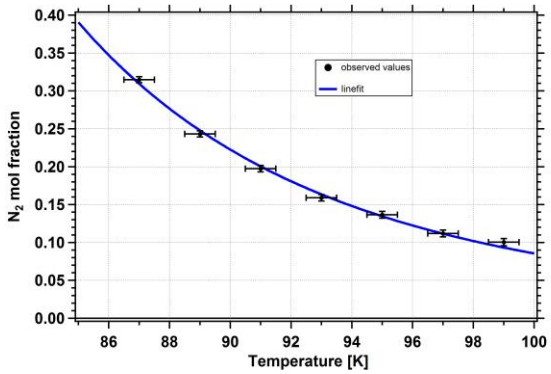

Figure 2. Laboratory measurement of mole fraction of nitrogen absorbed by pure methane at various temperatures at 1.5 bar.

In methane-ethane mixtures at a constant temperature and pressure, the amount of nitrogen dissolved was dependant on the ratio of ethane to methane. Lower molar fractions of ethane (thus higher methane molar fractions) allowed a larger amount of nitrogen to dissolve in the liquid mixture (Figure 3).

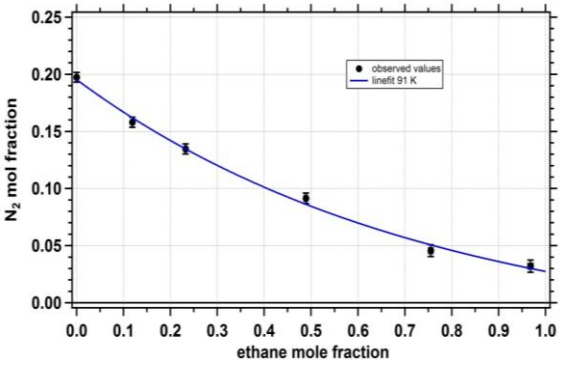

Figure 3. Amount of nitrogen absorbed versus ethane mole fraction at 91 K and 1.5 bar, at equilibrium.

From analysis of our experimental data, we were able to generate predicted curves of the amount of nitrogen that would dissolve in Titan lake fluids at various temperatures, compositions, and pressures. The predictions for 1.5 bar atmospheric pressure are shown in Figure 4. Our laboratory measurments can be used to further constrain theoretical and engineering models, and infer Titan lake properties and observations.

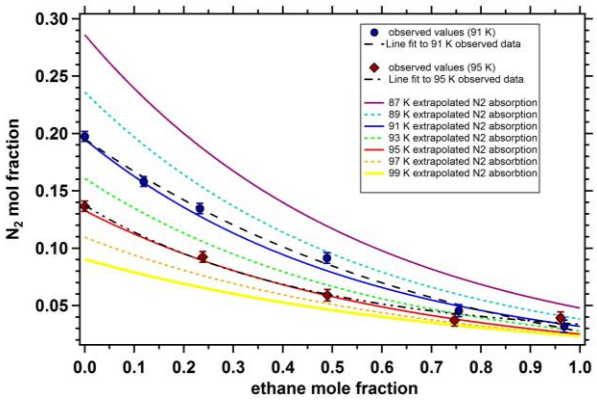

Figure 4. Predicted amounts of nitrogen absorption in varying methane-ethane mixtures at various temperatures at 1.5 bar. Points show laboratory measurements.

During our experimental work, we captured mages demonstrating that methane will not freeze under Titan conditions (Figure 5). Figure 5A shows solid methane in a methane atmosphere at 80 K. Once nitrogen gas is introduced, the nitrogen dissolves into the methane to create a liquid mixture at temperatures well below the freezing point of pure methane (Figure 5B) [10].

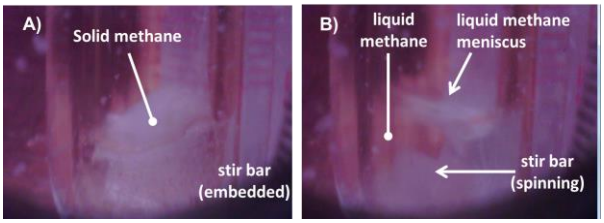

Figure 5. A) Endoscope view of pure frozen methane in a pressure vessel at 80 K (methane partial pressure <0.04 bar). Same material in a 0.7 bar atmosphere of nitrogen gas at 82.3 K. In B, the methane-nitrogen mixture is liquid and stirs freely. The white object is a stir bar for efficient agitation.

Implications: Titan rainfall and runoff fluids are predicted to be mostly methane [11] and will contain a large amount of dissolved nitrogen. However, as soon as the methane-rich runoff fluids mix with lake mixtures containing appreciable ethane, the solubility of nitrogen decreases and the excess nitrogen gas exsolvates out, likely in the form of bubbles. Our work allows us to calculate the amount and the volume of nitrogen gas released. For rainfall fluids entering a lake containing 0.5 mole fraction ethane (a possible Ontario Lacus composition), over 15x the equivalent volume of entering fluid will be released as gaseous nitrogen. That's a lot of bubbles!

Nitrogen exsolvation is endothermic. Since less nitrogen is contained at higher temperature, on warming, nitrogen will exsolve. The overall effect of exsolvation will be to cool a Titan lake during nitrogen release.The opposite effect occurs on cooling lake fluids: more nitrogen dissolves, warming the lake. Thus, due to nitrogen solvation/exsolvation, Titan lakes will be more thermally stable than expected for pure hydrocarbon fluids alone This effect is strongest with methane-rich fluids at lower temperatures. In laboratory practice, we use this effect to create thermally stable cryogenic baths between 80 – 90 K.

A large amount of dissolved nitrogen will also affect the effective heat capacity (C_p) of the liquid mixture as any thermal energy put into a Titan lake fluid will be buffered by nitrogen exsolvation. This implies that the thermal load from a potential Titan lake lander may generate significant nitrogen bubbles around any heated surfaces that contact Titan lake fluids, creating an exsolvation version of the Leidenfrost effect, (responsible for the vapor jacket created when plunging a warm object into liquid nitrogen).

Conclusions: We obtained laboratory measurements of molar fractions of ethane, methane, and nitrogen at Titan-relevant temperatures and pressures. We find nitrogen dissolution to be significant for methane-rich cryogenic fluids. The effects of nitrogen dissolution and exsolvation have important implications for Titan lakes thermal stablitity, bubble formation, and future lake lander missions.

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